

**REMARKS**

Claims 1-17 and 24-25 are currently pending in this application. Claims 1-8, 10-17 and 24-25 are currently amended.

**Claim Amendments**

Claims 1-8, 10-17 and 24-25 of the application are hereby amended to recite that the carbon structure through which the catalyst moves is a one-dimensional structure. These amendments are being undertaken to provide further clarity to the claimed subject matter, and are fully supported in the specification as filed, for example, on page 10 at lines 9-13 of the English language specification.

**Claim rejections**

Claims 1-17, 24, and 25 are rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the written description requirement. This rejection is traversed.

The Examiner states that at the time the application was filed, the specification does not support the claimed invention because there is no support for the formation of nanotubes. This is incorrect. Figure 1 is a schematic representation of the production of a carbon nanotube. The diagrams are fully supported in the specification beginning on page 13 (first embodiment) and continuing through page 19. The Applicant clearly refers to electron scanning micrographs which confirmed the formation of a carbon nanotube (pg 18 lines 26- pg 19, line 2, and pg 19 lines 6-9).

In addition, Applicant herewith attaches an article published by the inventors Ishida, Ochiai and Fujita ("In situ Observation of Carbon-Nanopillar Tubulization Caused by Liquidlike Iron Particles", Physical Review Letters, 2004: vol. 92, no. 21, pp. 21502-1 to 21502-4). This publication describes the successful preparation of nanotubes using the methods described in the specification of the application as filed and claimed herein. In particular, Applicant draws Examiner's attention to the series of transmission electron micrographs presented in Figures 3 and 4, which show the growth of carbon nanotubes of the invention. Thus, Examiner's concern that there is "no evidence on the record of nanotube formation" has been addressed.

In summary, the specification does provide adequate support for the

formation of carbon nanotubes by a novel mechanism.

In view of the foregoing, Applicant respectfully requests reconsideration and withdrawal of this rejection.

Claims 1, 2, and 10 are rejected under 35 U.S.C. 102(b) as being anticipated by Uemura (US patent No: 6,239,547 B1). This rejection is traversed.

According to Uemura, there is provided a carbon nanotube (CNT) by DC arc discharge without using a catalyst. In this case, CNT growth is carried out while carbon as a raw material vaporizes and deposits again on one electrode in an ultra-high temperature field where a discharge between electrodes occurs.

In contrast, the method of the present invention utilizes a catalyst and is a method of solid-phase growth, and thus differs markedly from Uemura.

DC arc discharge using a catalyst is known as a method of producing CNTs. However, unlike the present method, it is a method of gas-phase growth and thus differs from the present invention, wherein CNTs are prepared by solid-phase growth by moving a catalyst substance in a previously prepared carbon structure.

In view of the foregoing, Applicant respectfully requests reconsideration and withdrawal of this rejection.

Claims 1, 2, 5, 6, 10, 13, 14 are rejected under 35 U.S.C. 103 (a) as being unpatentable over Uemura in view of Fujita (2001 American Vacuum Society). This rejection is traversed.

The distinctions between Uemura and the present invention are discussed above. Applicant submits that one of skill in the art would recognize that solid-phase growth is different than gas-phase growth by DC arc discharge as taught by Uemura in the mechanism of CNT growth. In addition, Applicant submits that one of skill in the art would recognize that CNTs cannot grow in a gas-phase growth process that includes a vapor and re-deposit process as taught by Fujita because it would be impossible to maintain a suitable density of energy and a suitable density of particles in a reaction area by making the size as small as is described.

Therefore, Fujita does not cure the defects of Uemura as a reference, and the combination of Fujita with Uemura does not render the subject matter of the present invention obvious.

In view of the foregoing, Applicant respectfully requests reconsideration

and withdrawal of this rejection.

Claims 1- 4, 8- 10, and 17 are rejected under 35 U.S.C. 103 (a) as being unpatentable over Uemura and Fujita, and in further view of Ota (US patent application 2005/0245390 A1). This rejection is traversed.

As discussed above, a hypothetical combination of Uemura and Fujita does not anticipate or make obvious the present invention.

Ota teaches a catalyst that is used for fuel cells in order to dissolve the fuels thereof. Applicant notes that platinum (Pt) is used in all of the examples of Ota. The carbon fibers are used as a battery electrode to fix the Pt catalyst. As such, the catalyst of Ota is completely unable to influence the structure and/or behavior of the carbon fibers. In addition, according to Ota, the Pt catalyst is precipitated from a chloroplatinic acid solution by a reduction reaction (see Examples 1-4). One of skill in the art would readily recognize that once the Pt is precipitated and has become a catalyst, there is neither liquefaction nor moving of the Pt during the 400 °C heat drying due to the high melting point of Pt. The heat treatment in the range of 600-3000 degrees is used by Ota only for growth of carbon fibers used for an electrode, or simply as a heat treatment after carbon fiber growth. Therefore, the use of these elevated temperatures is not related to the Pt catalyst which is formed after the heat treatments. It is thus impossible to derive information regarding CNT growth from Ota.

Ota does not cure, mitigate, or even address the defects of Uemura in view of Fujita, and no combination of Ota with Uemura and Fujita (or any other reference) renders the subject matter of the present invention obvious.

In view of the foregoing, Applicant respectfully requests reconsideration and withdrawal of this rejection.

Claims 1, 2, 10-12 are rejected under 35 U.S.C. 103 (a) as being unpatentable over Uemura and Fujita, and in further view of Ota (US patent application 2005/0245390 A1). This rejection is traversed.

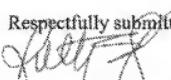
The deficiencies of the hypothetical combination of Uemura and Fujita are discussed in detail above, as are the lack of Ota to cure or mitigate in any way these defects. To reiterate, the carbon fibers of Ota are used as a battery electrode to fix the Pt catalyst. As such, any catalyst employed by Ota is not able to influence the structure and/or behavior of the carbon fibers. In contrast, in the

present invention, the catalyst moves within a carbon structure thereby forming a trail region corresponding to the path of the catalyst, which crystallizes in the wake of the catalyst, forming a carbon nanotube. Ota does not cure the marked deficiencies of the hypothetical combination of Uemura and Fujita, and the combination of Ota with Uemura and Fujita does not render the subject matter of the present invention obvious.

In view of the foregoing, Applicant respectfully requests reconsideration and withdrawal of this rejection.

A provisional petition is hereby made for any extension of time necessary for the continued pendency during the life of this application. Please charge any fees for such provisional petition and any deficiencies in fees and credit any overpayment of fees to Attorney's Deposit Account No. 50-2041.

Respectfully submitted,



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## In situ Observation of Carbon-Nanopillar Tubulization Caused by Liquidlike Iron Particles

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The sublimation process of amorphous carbon nanopillars was observed *in situ* by transmission electron microscopy. Amorphous carbon nanopillars were transformed into graphitic tubulites by annealing at 650–900°C in the presence of iron nanoparticles. A molten catalyst nanoparticle penetrated an amorphous carbon nanopillar, dissolving it, and leaving a graphite track behind. An iron nanoparticle moved with its shape changing like an earthworm. We concluded that the tubulization mechanism is a solid-(quasi)liquid-solid mechanism where the carbon phase transformation is a kind of liquid phase graphitization of amorphous carbon catalyzed by liquefied metal–carbon alloy nanoparticles.

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Carbon nanotubes [1-3] are currently the focus of intense research because of their unique properties and potential to impact broad areas of science and technology. However, despite the enormous progress in nanotube synthesis [4-6], the carbon nanotube growth mechanisms are still being searched for because there have been no direct observations of the carbon nanotube growth process. Here we report on our *in situ* observation of the tubulization process of amorphous carbon nanopillars by transmission electron microscopy.

Figure 1 shows our sample preparation method. First, we deposited an iron-doped amorphous carbon foundation, which was about 1  $\mu\text{m}$  thick, on a molybdenum grid for the transmission electron microscope (TEM) through focused-ion-beam-induced chemical vapor deposition [7] using ferrocene ( $\text{Fe}(\text{C}_{10}\text{H}_{10})_2$ ) gas source [8] injected through a nozzle. Next, we grew amorphous carbon pillars, which were 10–100 nm in diameter and 100–500 nm long, on the iron-doped carbon foundation through electron-beam-induced chemical vapor deposition [9] in a phenanthrene ( $\text{C}_{14}\text{H}_{10}$ ) gas ambient [10]. Figure 1(c) shows a scanning electron micrograph of a prepared sample.

The molybdenum grid, on which the iron-doped carbon foundation with the amorphous carbon nanopillars was grown, was set on a heating stage of an ultrahigh-vacuum (UHV) TEM (JEOL 2000FXVII). The UHV-TEM was equipped with a video camera [11]. The graphitization process of the amorphous carbon pillars was observed *in situ* by UHV-TEM operated at 200 eV and was recorded on videotape at a TV-rate time resolution.

Figure 2(A) shows a sketch of the pillar in each annealing stage. The specimen holder was heated and kept at 600°C until the draft of the specimen holder stopped (about 2 h). During this process, the electron beam intensity was decreased to about 0.1 A/cm<sup>2</sup> (about 1/1000 of the high-resolution TEM observation condition) to

avoid electron beam damage to the carbon nanopillars. When the temperature of the specimen reached about 600°C, iron particles about 2 nm in size appeared in the iron-doped carbon foundation immediately. Because of the coalescence of the particles, the size of the iron

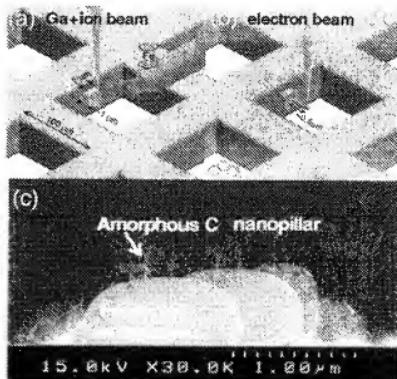


FIG. 1 (color). Schematic diagram of the sample preparation method. (a) An iron-doped amorphous carbon foundation was deposited on a molybdenum grid for the transmission electron microscope (TEM) through focused-ion-beam-induced chemical vapor deposition using a ferrocene ( $FeC_{10}H_{10}$ ) gas source injected through a nozzle. (b) Amorphous carbon pillars were grown on an iron-doped carbon foundation by electron-beam-induced chemical vapor deposition in a phenanthrene ( $C_{14}H_{10}$ ) gas ambient. (c) A scanning electron micrograph of a prepared sample.

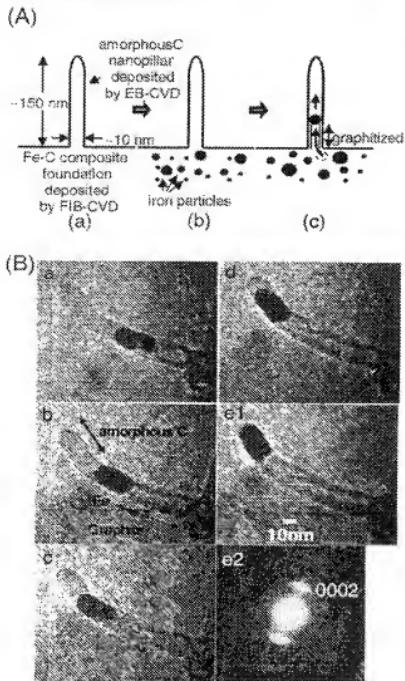


FIG. 2. (a) A sketch of the pillar in each annealing stage: (a) A prepared sample. (b) A sample was heated at 600 °C. Iron-carbon alloy particles appeared in the foundation within a few minutes. (c) A sample was heated at 650 °C. An iron-carbon alloy particle was sintered into a carbon nanopillar and graphitization started from the bottom of the pillar. (B) A series of transmission electron micrographs, recorded from videotape at 2-s time intervals, showing the graphitization process of an amorphous carbon nanopillar about 10 nm in diameter at about 650 °C. An electron diffraction pattern (e2) shows that the pillar had a graphitic structure.

particles increased to 10 nm in a few minutes [Fig. 2(A)-(b)]. When the drift of the specimen holder stopped, the temperature of the specimen holder was raised from 600 to 650 °C. Though the specimen holder again began drifting slowly, the image of the specimen could still be monitored by the UHV-TEM camera. An iron particle

moved toward the bottom of a pillar and sintered into the pillar [Fig. 2(A)-(c)]. The particle changed its shape and size much like a liquid while moving in the pillar. This liquidlike particle moved through the inside of the carbon nanopillar and left behind a graphitic track.

Figure 2(B) shows a series of electron micrographs, reproduced from videotape at 2-s time intervals, taken from a 10-nm-diameter carbon nanopillar at about 650 °C. The iron-carbon alloy particle moved from the bottom toward the top of the pillar. Once it reached the top of the pillar, the particle stopped moving. The mean speed of the iron-carbon alloy particle was about 8 nm/s. Figure 2(B)-(e2), an electron micrograph corresponding to Fig. 2(B)-(e1), shows an electron diffraction pattern taken from the carbon nanopillar. This revealed that the carbon nanopillar had a graphitic structure. The carbon nanopillar was transformed into a multiwalled (about ten layers) carbon nanotube by this heating process. However, the nanotube was not straight and contained some defects. We thought that these defects were caused by fluctuation in the moving speed of the iron-carbon alloy particle and in the particle diameter. A molten catalyst nanoparticle penetrated the amorphous carbon nanopillar, dissolving it and precipitating carbon atoms at the tail of the nanoparticle. These atoms arranged themselves into a graphene sheet. The equilibrium eutectic temperature of the corresponding iron-carbon alloy is 1150 °C. The temperature of 650 °C, at which the catalyst particles acted as a liquid in this experiment, was extremely low by comparison. It is well known that the melting points of nanometer-sized particles are much lower than those of the corresponding bulk materials [12]. Considering the size effect, the equilibrium eutectic temperature of a 10-nm-particle-size alloy is reduced to 1000 °C. On the other hand, Yudasaka *et al.* reported that the lowest temperature at which carbon diffuses into a 10-nm-thick iron film and recrystallizes as graphite is about 500–600 °C [13].

A series of electron micrographs, reproduced from videotape [14] at 1-s time intervals, of a 10-nm-diameter carbon nanopillar at about 650 °C is shown in Fig. 3(A). The iron-carbon alloy particle moved from the bottom toward the top of the pillar with its shape changing like a liquid. These shape changes, between the shrunk shape of the tail and elongated shape of the top, are repeated like an earthworm. When the catalyst particle moved at constant speed, the graphitic tube structure was formed. If the tail of the particle stayed at the same place for a few hundred milliseconds, the graphene sheet closed to make a cap within the nanotube (arrows 1 and 2). The precipitation interface between the graphitic tube and the catalyst particle (indicated by arrowheads) had a flat shape. TEM images of the moving catalyst particle showed sometimes diffraction contrast, which revealed that the particle had crystalline nature. The concept of the quasi-solid state, which is neither solid nor liquid, has been

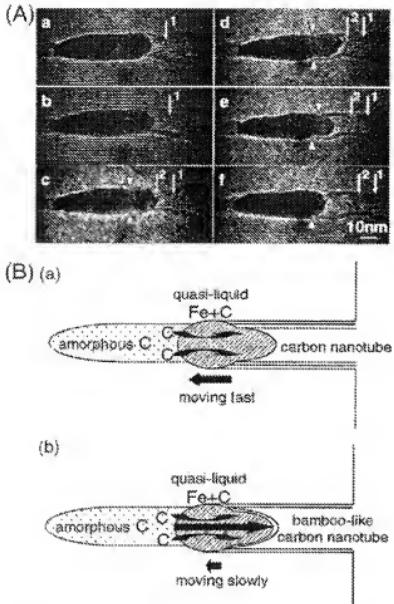


FIG. 3. (A) A series of electron micrographs, reproduced from videotape, at 1-s time intervals, taken from a 10-nm-diameter carbon nanopillar at about 650 °C, and (B) a model of the carbon nanotube growth mechanism. Arrowheads indicate the precipitation interface between the graphitic tube and catalyst particle. Arrows 1 and 2 indicate the bamboo-like structures. The catalyst particle moved smoothly (a) and not smoothly (b).

proposed for nanometer-sized particles [15]. These catalyst particles are considered quasisolid particles.

Corresponding models of this carbon nanotube growth mechanism are shown in Fig. 3(B). When the penetrating speed of the catalyst particle is constant [Fig. 3(B)-(a)], precipitating carbon incorporates at the edges of the growing nanotube. When the penetrating speed of the catalyst particle is 0 for a few hundred milliseconds [Fig. 3(B)-(b)], the precipitating carbon incorporates into a graphitic cap and a bamboo-like structure forms [16]. Our observations suggest that carbon atoms, which are supplied from a dissolved carbon nanopillar, diffuse through the surface layer of a catalyst particle. Based on

molecular dynamics simulations, Shibuta *et al.* proposed that a graphene sheet is formed inside the surface of a catalyst particle [17]. We thought that the motive force of the catalyst particle was caused by the difference between the solubility of amorphous carbon in iron and that of graphite carbon in iron. Another possible cause of the motive force is that there were temperature gradients in the nanopillar and nanoparticle.

In a thick pillar case (about 100 nm in diameter), graphitization occurred partially. The temperature was about 900 °C. Figures 4(a) and 4(b) were reproduced from the videotape. The catalyst particle, about 10 nm in diameter, was smaller than the diameter of the pillar. A catalyst iron-carbon alloy particle, indicated by an arrowhead, moved rapidly inside the pillar in a random direction and transformed the amorphous carbon into the graphite track. The maximum speed of the catalyst particle was about 500 nm/s. The shape of the catalyst particle was changing, and the particle sometimes broke up and left small catalyst particles (indicated by arrows). The graphite track was clearly observed in Figs. 4(c) and 4(d) [enlarged image of 4(c)-(A)], which was taken at room temperature after annealing.

Our observation results indicate that the tubulation mechanism is a solid-(quasiliquid)-solid mechanism where the carbon phase transformation is a kind of liquid phase graphitization of amorphous carbon catalyzed by liquefied metal-carbon alloy nanoparticles [18,19]. The low-temperature liquefaction of catalyst particles causes the principal difference compared to the synthesis of carbon nanofibers, which are usually catalyzed by solid

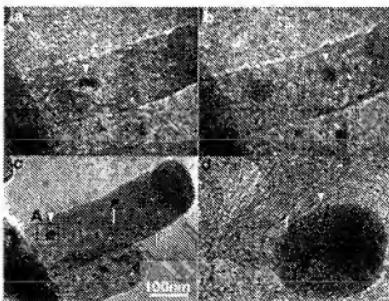


FIG. 4. A series of transmission electron micrographs showing the graphitization process of a carbon nanorod about 100 nm in diameter at about 900 °C. (a) and (b) were reproduced from the videotape. (b) was taken 1 s after (a). (c) was taken at room temperature after annealing. (d) is an enlarged image of the region A indicated in (c).

catalysts of similar composition in a related graphitization process.

Carbon and metal catalyst composite nanopillars can thus be fabricated at any place, in any direction, at any length, and in any thickness by using nanofabrication and heat treatment at a temperature below the equilibrium eutectic temperature of the corresponding iron-carbon alloy (1150 °C). Therefore, we should be able to synthesize carbon nanotubes of any desired size at any desired location.

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- [14] See EPAPS Document No. E-PRLTAO-92-015620 for a series of electron micrographs, reproduced from videotape. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp:aip.org> in the directory /epaps/. See the EPAPS homepage for more information.
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